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Canadian Journal of Chemistry
Revue canadienne de chimie

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Journal:	*Canadian Journal of Chemistry*
Manuscript ID	cjc-2015-0576.R1
Manuscript Type:	Article
Date Submitted by the Author:	10-Mar-2016
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Keyword:	Europium complex, luminescence, 2,2'-bipyridine, DTTA, ditopic ligand

Graphical Abstract

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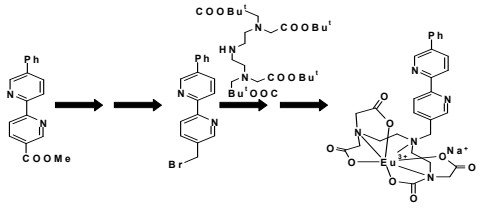
Dmitry S. Kopchuk, Dmitry E. Pavlyuk, Igor S. Kovalev, Grigory V. Zyryanov, Vladimir L. Rusinov, Oleg N. Chupakhin



Synthesis of a new DTTA- and 5-phenyl-2,2′-bipyridine-based ditopic ligand and its Eu^{3+} complex

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Abstract

New diethylenetriamine-N,N,N'',N''-tetraacetate (DTTA) - and 5-phenyl-2,2′-bipyridine-based ditopic ligand has been synthesized. The improved method for the synthesis of DTTA *tert*-butyl ester has been developed. The water-soluble Eu^{3+}*DTTA complex of this ligand has been prepared, and its photophysical properties have been studied. Due to the presence of an extra chelating unit, namely 5-phenyl-2,2′-bipyridine, this Eu^{3+}*DTTA complex demonstrated the strong fluorescence response to the Zn^{2+} cation (fluorescence enhancement) and the simultaneous fluorescent and phosphorescent response (fluorescence and phosphorescence quenching) to the Cu^{2+} or Ni^{2+} cations in aqueous solutions.

Key words: Europium complex, luminescence, 2,2'-bipyridine, DTTA, ditopic ligand.

Introduction

Today lanthanide (III) cations complexes are of great interest due to their wide applications. They can be used in medicine[1] due to the generation of radiation in the near-

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infrared,[2] as dyes for laser systems,[3] and as imaging agents for MRI.[4] Luminescent in the visible spectrum lanthanide complexes are heavily used as electroluminescent materials for OLEDs[5] and phosphorescent labels for bioimaging.[6]

Among the lanthanide complexes containing aromatic moiety (antenna) there are two main types of the ones: in the first case, the antenna is involved in the coordination of the lanthanide cation, in the second case an antenna group separated from the metal center by a spacer group does have a connection to the lanthanide cation through the spacer bounds.[7] The complexes of the second type are used, for example, as chemosensors for a number of metal cations. E.g., in these complexes dipicolylamine fragments or their analogues are usually used for the coordination with target analytes.[8] Polyaminocarboxylic acids, such as cyclen derivatives, are usually used for lanthanide cation complexation. There are also examples of di- or polytopic ligands based on oligopyridines where oligopyridines are used as a separated center for the metal cation complexation. Polynuclear complexes of these ligands are used for various purposes,[9] for example as MRI agents.[10]

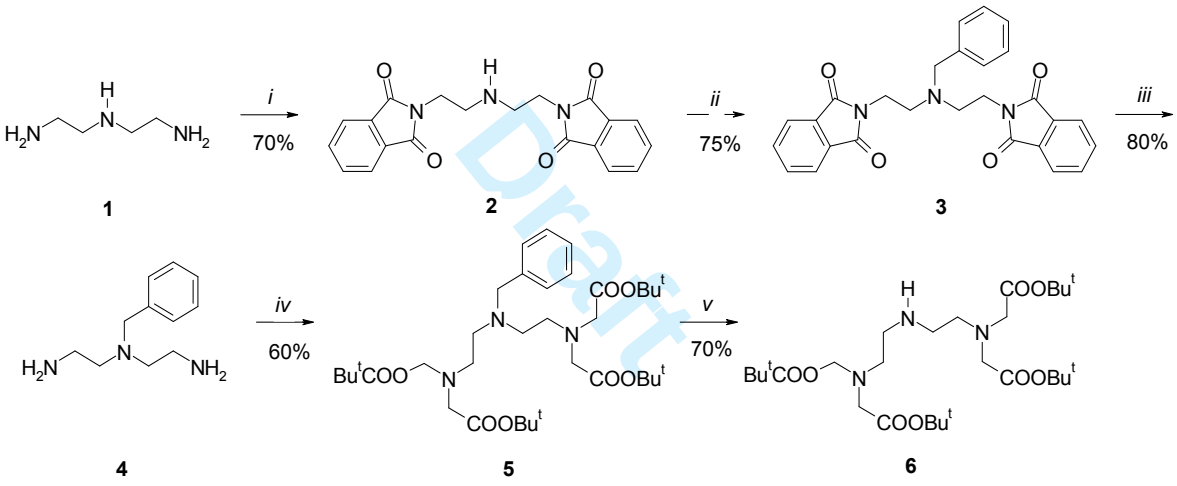
In this paper, we propose a versatile synthetic approach towards ditopic ligand based on 5-phenyl-2,2′-bipyridine chromophore and bearing the binding site for a lanthanide cation, which is separated by a methylene bridge from 2,2′-bipyridine system.

Results and Discussion

In order to prevent the participation of 2,2′-bipyridine system in the lanthanide complexation the lanthanide binding site is attached at the position C5′ of 2,2′-bipyridine system. In this case the choosing of the chromophore is determined by its acceptable photophysical characteristics. In particular, it has an acceptable absorption maximum, i.e. 300-305 nm, depending on the solvent, which is in a sharp contrast to the non-substituted 2,2′-bipyridine system.[11] Furthermore, it was reported previously that 5-aryl-substituted 2,2′-bipyridines can be successfully used for the sensitization of europium luminescence, and

based on 6′-DTTA-methyl or 6′-DO3A-methyl-substituted compounds the corresponding europium complexes were isolated and their photophysical properties were studied.[12] Also it should be noted that based on commercially available starting materials convenient methods for synthesis of the 5-aryl-2,2′-bipyridines, including 5′-substituted, were previously developed.[11]

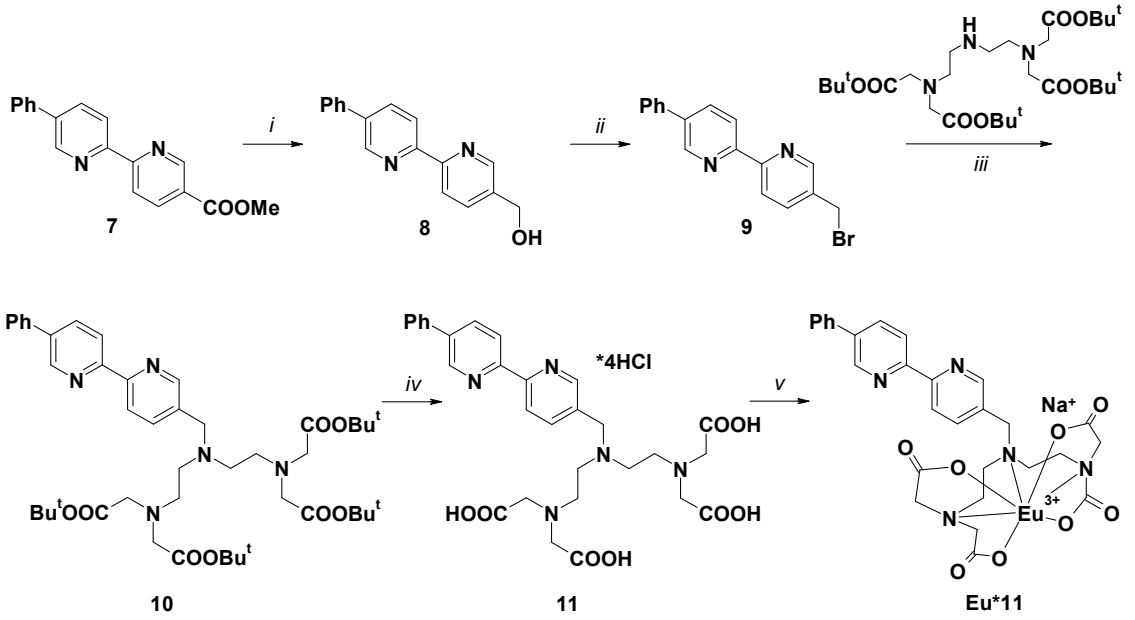
We chose the DTTA moiety for a lanthanide cation chelating. This choice is due to its greater availability compared with cyclic analogues and comparable luminescence efficiency that has also been reported in literature.[12] The DTTA ester was prepared by starting from the commercially available diethylenetriamine **1** according to the modified method[13] (Scheme 1).



Scheme 1. The Synthesis of tetra-*tert*-butyl ester of DTTA. Reagents and conditions: *i*) phthalic anhydride, CH_3COOH, 118 °C, 1 h; *ii*) $PhCH_2Br$, DMF, 20 °C, 12 h; *iii*) hydrazine hydrate, EtOH, 78 °C, 25 h; *iv*) *tert*-butyl bromoacetate, DMF, 20 °C, 12 h; *v*) ammonium formate, Pd / C, MeOH, 65 °C, 2 h.

The first three steps of the synthesis were performed as described previously.[13, 14] The preparation of compound **5** as a further step was also described previously,[13] but no detailed synthetic procedure was reported, therefore this method was modified. Intermediate **5** was purified initially by flash chromatography, where we have found that amine **5** can be used as

it is and after the cleavage of benzyl group the final amine **6** can easily be purified by flash chromatography. In addition, for the removal of the benzyl protection we used an alternative technique: reaction of **5** with ammonium formate as source for the *in situ* hydrogen generation in the presence of palladium on charcoal in methanol under refluxed conditions. Total yield after two stages was up to 55%, and no column chromatography is needed.



Scheme 2. The preparation of the target ligand. Reagents and conditions: *i*) $NaBH_4$, EtOH / $CHCl_3$ (8:1), 70 °C, 6 h then $NaBH_4$, EtOH, 78 °C, 4 h; *ii*) PBr_3, $CHCl_3$, r.t., 10 h, then 61 °C, 2 h; *iii*) K_2CO_3, acetonitrile, 82 °C, 10 h; *iv*) HCl (5N), r.t., 12 h, then HCl (11N), r.t., 2 h, then acetonitrile, r.t., 8 h; *v*) NaOH, water, r.t., then $EuCl_3*6H_2O$, water r.t., 2 h.

Prepared as described earlier[11] 5′-methoxycarbonyl-5-phenyl-2,2'-bipyridine **7** was used as a building block for the construction of the heterocyclic core (Scheme 2). Thus, the reduction of ester **7** with sodium borohydride afforded the hydroxymethyl derivative **8** (Scheme 2). It was found that upon carrying out the reaction in the common conditions, i.e. in refluxing ethanol, compound **8** was isolated as a minor product in 40% yield. This is due to the competitive reaction of the ester hydrolysis: the corresponding carboxylic acid **8a** was

isolated as a major product after the quenching of the reaction mixture with water and acidifying of the aqueous phase with hydrochloric acid. The solubility of the starting ester **7** in ethanol is low, and in order to increase the degree of conversion of **7** to the desired product **8** the mixture of chloroform-ethanol (1:8) was used as a reaction media. As a result the reaction yield has been improved to 69%. Bromomethylbipyridine **9** was obtained by the reaction of alcohol **8** with phosphorus tribromide.

Further reaction of compound **9** with the DTTA ester in the presence of base in refluxing dry acetonitrile afforded the compound **10** as a precursor of the title ligand. The product **10** was separated from the side product, 5-hydroxymethylbipyridine **8**, by column chromatography. The target ligand **11** was obtained as a hydrochloric salt upon the removal of the *tert*-butyl protection by 5N hydrochloric acid at room temperature.

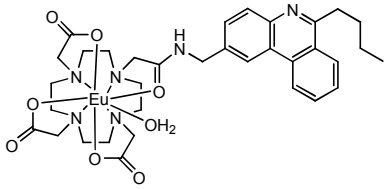
In order to obtain the europium **Eu*11** complex the *in situ* prepared tetrasodium salt of the ligand **11** was subjected to react with europium chloride in aqueous solution. As a hard Lewis acid the europium cation preferably forms a complex by interacting with a polyamine moiety of the new ligand. This is supported by a lower absorption maximum as compared with complexes of Eu and 5-phenyl-2,2'-bipyridine, having a secondary chelating site at the position 6′, where bipy unit is involved in the coordination of Eu cation (304 nm instead of 327 nm).[12] Besides the phosphorescence of the europium cation (the phosphorescence quantum yield is 0.0034; phosphorescence spectrum is shown in Fig. 1), the complex **Eu*11** demonstrates the significant fluorescence of aryl-bipyridine unit (all the measurements have been carried out at pH = 7) due to the radiative transitions S1 → S0 of phenyl-bipyridine moiety[7]. Due to the fact that energy transfer from the *bipy* moiety to the europium cation is not very efficient in this case, the probability of the generation of fluorescence significantly increases, which explains its rather high quantum yield (0.125).

The number of water molecules presented in the Eu first coordination sphere (q) was calculated by the comparison of the phosphorescence lifetime of europium **Eu*11** complex in water (τ_{H2O}) and deuterated water (τ_{D2O}) by the following formula[15]:

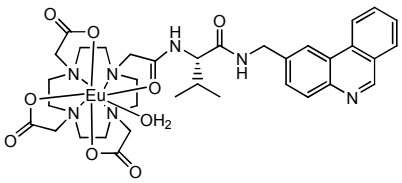
$q = 1.11*(1/\tau_{H2O} - 1/\tau_{D2O} - 0.31)$

Based on this formula it was calculated that two water molecules are present in the coordination sphere of the Eu cation which is also correspond to the claimed structure. The photophysical properties of the europium **Eu*11** complex are summarized in Table 1. In addition, the structure of the complex **Eu*11** was also confirmed based on the data of elemental analysis and the ES-MS: the isotope distribution of main peaks fits to a calculated isotope values.

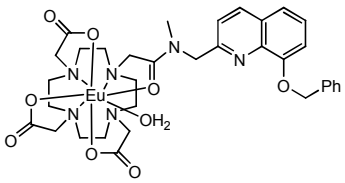
For the comparison of the photophysical properties, some previously published[16, 17] Eu^{3+} complexes **Eu*12-Eu*14** with antenna moiety separated from the cation chelates by spacer groups have been added to the Table 1. Based on these data one may conclude that the herein reported complex **Eu*11** and previously reported complexes **Eu*12-Eu*14** have similar photophysical characteristics, namely their phosphorescence quantum yields and phosphorescence lifetime values are close.



Eu*12



Eu*13



Eu*14

Table 1. Photophysical properties of europium complexes **Eu*11-Eu*14** in an aqueous solution at room temperature

Complex	Absorption maximum, λ_{max}, nm	ε (dm^3* mol^{-1}*cm^{-1})	Φ^a	τ^b_{H2O}, ms	τ^c_{D2O}, ms	q^d
Eu*11	304	7950	0.0034	0.369	1.734	2.02

Eu*12[e]	293, 330, 345	6000, 2500, 2500	0.014	-	-	0.92
Eu*13[e]	295, 330, 347	6700, 2200, 2200	0.0038	-	-	0.89
Eu*14[f]	243, 302	-	0.002	0.72	2.6	0.88

[a]Phosphorescence quantum yield (calculated using $[Ru(bpy)_3]Cl_2$ as a reference[18]); [b]phosphorescence life time in water solution; [c]phosphorescence life time in D_2O solution; [d]the calculated parameter corresponding to the number of water molecules in the first coordination sphere of the europium cation; [e]according to the literature data[16]; [f]according to the literature data[17]

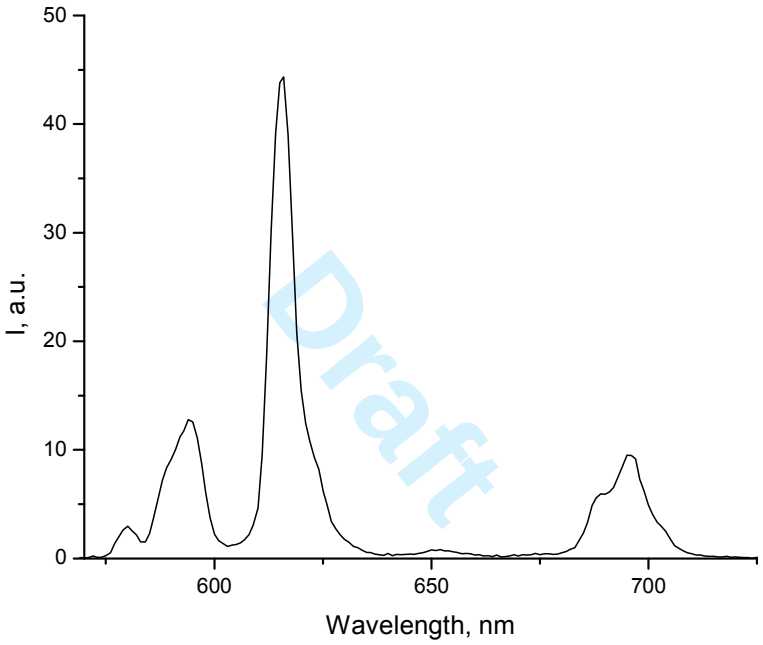


Fig. 1. Phosphorescence spectra of **Eu*11** complex

In an aqueous solution **Eu*11** complex shows a luminescent response to a number of metals cations. In particular, the addition of zinc perchlorate (3 eq.) causes a significant enhancement of the fluorescence, accompanied by the slight bathochromic shift of the fluorescence spectrum maximum (Fig. 2). Up to 4-fold enhancement of the fluorescence intensity of the bipyridine fluorophore is observed (from 0.125 to 0.53). The same phenomenon has previously been described for the "naked" 5-phenyl-2,2′-bipyridine, i.e. with

no DTTA or Eu*DTTA attached, and it can be explained by a significant contribution of n-π-transition to the excited state of the phenylbipyridine chromophore.[19] It is worthy to mention that the phosphorescence of the **Eu*11** complex was not affected mainly: upon the addition of $Zn(ClO_4)_2$ we have not observed any significant changes in the intensity of the phosphorescence or any shift of the phosphorescence spectrum maxima.

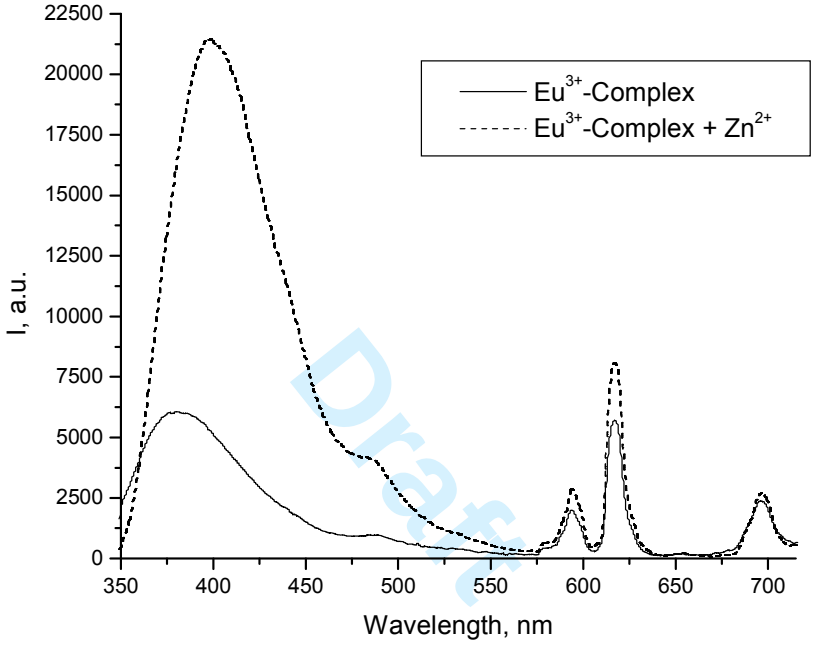


Fig. 2. The luminescence of on aqueous solution of **Eu*11** complex before (solid line) and after (dotted line) the addition of $Zn(ClO_4)_2$ (3 eq.) with no delay time

In contrast, the addition of Cu^{2+} or Ni^{2+} salts caused the significant quenching of both fluorescence and phosphorescence of the **Eu*11** complex (Fig. S1-S2, Supplementary Information). It worth to mention that the photoluminescence quenching of both oligopyridines[11] and their Eu^{3+} complexes[20] in the presence of Cu^{2+} or Ni^{2+} salts is quite common and can be explained by either static interactions[21] or energy transfer processes[21]. At the same time some emissive heterodinuclear complexes of Ni^{2+} and Eu^{3+} are reported.[22]

Conclusions

In summary, a convenient method for the preparation of the DTTA ester and its 5-phenyl-2,2′-bipyridine-appended ligand has been developed. The Eu^{3+}*DTTA complex of this ligand due to the presence of available for the chelating of metal cations 5-phenyl-2,2′-bipyridine unit demonstrated the strong fluorescence response to the Zn^{2+} and the simultaneous fluorescent and phosphorescent response to the Cu^{2+} or Ni^{2+} cations in aqueous solutions.

Experimental Section

Gerenal Procedures

All common reagents and solvents were used from commercial suppliers without further purification. Melting points were determined with a Boetius apparatus. ^{1}H NMR spectra were acquired on a Bruker Avance II spectrometer (400 MHz), 298 K, digital resolution ± 0.01 ppm, using TMS as internal reference. Mass-spectra were recorded on MicrOTOF-Q II (Bruker Daltonics), electrospray as a method of ionization. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrometer. Luminescence spectra were recorded on a Varian Cary Eclipse fluorimeter. Starting compounds: 5′-methoxycarbonyl-5-phenyl-2,2'-bipyridine,[11] bis(2-phtalylaminoethyl)amine,[14a] bis(2-phtalylaminoethyl)benzylamine,[13] bis(2-aminoethyl)amine[14b] were synthesized according to the described methods.

1,1,7,7-Tetrakis(*tert*-butyloxycarbonylmethyl)-1,4,7-triazaheptane (6). A mixture of bis(2-aminoethyl)benzylamine **4** (3.4 g, 17.59 mmol), anhydrous potassium carbonate (12.16 g, 87.95 mmol) and *tert*-butylbromoacetate (12.99 ml, 87.95 mmol) was stirred at r.t. in dry DMF (60 ml) for 12 h under argon atmosphere. After completion the solvent was removed under reduced pressure; inorganic compounds were dissolved in water (50 ml). The product was extracted with chloroform (2 x 100 ml). The extract was dried with anhydrous sodium sulfate; solvent was removed under reduced pressure. The residue was purified by flash chromatography (eluent: ethylacetate). The obtained alkylated benzylamine **5** without additional purification was dissolved in methanol (60 ml). Ammonium formate (4.29 g, 68.09 mmol) and palladium on activated carbon (10%) (725 mg) were added and the resulting

mixture was stirred under reflux for 2 h under argon atmosphere. The solids were filtered off and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (eluent: ethylacetate, then ethanol) to give the product **6** as yellow oil. Yield 5.41 g (9.67 mmol, 55%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 1.45 (s, 36H, Bu^t), 3.04 (t, 4H, ^3J = 5.6 Hz, $NHC\underline{H}_2CH_2$), 3.22 (t, 4H, ^3J = 5.6 Hz, $NHCH_2C\underline{H}_2$), 3.51 (s, 8H, $C\underline{H}_2COOBu^t$), 8.56 (s, 1H, NH). **ESI-MS** (acetonitrile), *m/z*: 560.39 $(M+H)^+$.

Starting method for the synthesis of 5′-hydroxymethyl-5-phenyl-2,2′-bipyridine (8). Ester **7** (1 g, 3.45 mmol) was suspended in ethanol (100 ml), $NaBH_4$ (0.65 g, 17 mmol) was added to that and the resulting mixture was refluxed for 4 h. Then additional portion of $NaBH_4$ (0.33 g, 8.5 mmol) was added and the resulting mixture was refluxed for 2 h. Water (100 ml) was added to that reaction mixture and the product **8** was extracted with DCM (3 x 75 ml). The extract was dried with anhydrous sodium sulfate. Solvents were removed under reduced pressure. The product **8** was used in the next step without additional purification. Yield 0.36 g (1.38 mmol, 40%). M.p. 130-132 °C. **^{1}H NMR** (DMSO-d_6, δ, ppm): 4.60 (d, 2H, ^3J 5.6 Hz, $C\underline{H}_2OH$), 5.17 (t, 1H, ^3J 5.6 Hz, OH), 7.40 (m, 1H, Ph), 7.49 (m, 2H, Ph), 7.71 (m, 2H, Ph), 7.83 (dd, 1H, ^3J 7.9 Hz, ^4J 1.9 Hz, H-4'), 8.10 (dd, ^3J 8.3 Hz, ^4J 2.3 Hz, H-4), 8.39 (d, 1H, ^3J 7.9 Hz, H-3'), 8.47 (d, 1H, ^3J 8.3 Hz, H-3), 8.57 (d, ^4J 1.9 Hz, H-6'), 8.88 (d, ^4J 2.3 Hz, H-6). **ESI-MS** (acetonitrile), *m/z*: 263.12 $(M+H)^+$.

For obtaining 5-phenyl-2,2′-bipyridine-5′-carboxylic acid (**8a**) hydrochloric acid (5N) was added to the water phase to adjust pH = 2. The resulting precipitation was filtered off, washed with water and dried in vacuum. Yield 450 mg (1.62 mmol, 47%). M.p. > 250 °C. **^{1}H NMR** (DMSO-d_6, δ, ppm): 7.42-7.54 (m, 3H, Ph), 7.75 (m, 2H, Ph), 8.17 (dd, 1H, ^3J = 8.3 Hz, ^4J = 2.0 Hz, H-4), 8.38 (dd, 1H, ^3J = 8.1 Hz, ^4J = 1.9 Hz, H-4'), 8.53 (d, 1H, ^3J = 8.3 Hz, H-3), 8.56 (d, 1H, ^3J = 8.1 Hz, H-3'), 8.97 (d, 1H, ^4J = 2.0 Hz, H-6), 9.16 (d, 1H, ^4J = 1.9 Hz, H-6'), 13.10 (br. s., 1H, COOH). Found, %: C 73.82, H 4.19, N 9.92. **$C_{17}H_{12}N_2O_2$**. Calculated, %: C 73.90, H 4.38, N 10.14. **ESI-MS** (acetonitrile), *m/z*: 275.08 $(M-H)^-$.

Improved method for the synthesis of 5′-hydroxymethyl-5-phenyl-2,2′-bipyridine (8). Ester **7** (1 g, 3.45 mmol) was dissolved in mixture of ethanol and chloroform (8:1, 200 ml) and the resulting mixture was refluxed for 6 h with adding $NaBH_4$ each hour (each portion 0.13 g, 3.45 mmol). Solvents were removed under reduced pressure. Ethanol (300 ml) was added to the residue and the resulting mixture was refluxed for 4 h with adding $NaBH_4$ after each hour (one portion 0.13 g, 3.45 mmol). Ethanol (150 ml) was removed under

reduced pressure. Water (200 ml) was added to the residue and the product was extracted with DCM (3 x 100 ml). Extract was dried with anhydrous sodium sulfate. Solvents were removed under reduced pressure. The product was used in the next step without additional purification. Yield 0.62 g (2.38 mmol, 69%).

5′-Bromomethyl-5-phenyl-2,2′-bipyridine (9). Compound **8** (1.05 g, 4 mmol) was dissolved in chloroform (65 ml), PBr_3 (0.76 ml, 8 mmol) was added and the resulting mixture was stored at room temperature for 10 h. Then the mixture was refluxed for 2 h. The reaction mass was washed with saturated solution of K_2CO_3 (50 ml). The product was extracted with chloroform (3 x 50 ml). Extract was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure. The analytical sample was obtained by recrystallization (ethanol). Yield 0.99 g (3.04 mmol, 76%). M.p. 160-162 °C. **^{1}H NMR** (DMSO-d_6, δ, ppm): 4.73 (s, 2H, CH_2Br), 7.35-7.56 (m, 3H, Ph), 7.73 (m, 2H, Ph), 7.96 (dd, 1H, ^3J 8.3 Hz, ^4J 2.5 Hz, H-4), 8.13 (dd, 1H, ^3J 8.4 Hz, ^4J 2.4 Hz, H-4'), 8.43 (d, 1H, ^3J 8.3 Hz, H-3), 8.48 (d, 1H, ^3J 8.4 Hz, H-3'), 8.71 (d, ^4J 2.5 Hz, H-6), 8.91 (d, ^4J 2.4 Hz, H-6'). Found, %: C 62.72, H 4.00, N 8.41. **$C_{17}H_{13}BrN_2$**. Calculated, %: C 62.79, H 4.03, N 8.61. **ESI-MS** (acetonitrile), *m/z*: 325.03 $(M+H)^+$.

1,1,7,7-Tetrakis(*tert*-buthyloxycarbonylmethyl)-4-[(5′-phenyl-2,2'-bipyridine-5-yl)methyl]-1,4,7-triazaheptane (10). Bromomethylbipyridine **9** (0.65 g, 2 mmol), ester of DTTA **6** (1.18 g, 2.1 mmol) and anhydrous potassium carbonate (1.38 g, 10 mmol) were suspended in dry acetonitrile (90 ml). The resulting mixture was stirred under reflux in argon atmosphere for 10 h. Solvent was removed under reduced pressure. Water (30 ml) was added and the product was extracted with chloroform (2 x 35 ml). Extract was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure. The product was isolated from residue by column chromatography (acetonitrile as eluent, *Rf* 0.2). The product was obtained as light yellow oil. The product was used in the next step without additional purification. Yield 0.48 g (0.6 mmol, 30%). **^{1}H NMR** ($CDCl_3$, δ, ppm): 1.43 (s, 36H, Bu^t), 2.69 (t, 4H, ^3J 7.0 Hz, bipy-$CH_2NC\underline{H}_2CH_2$), 2.88 (t, 4H, ^3J 7.0 Hz, bipy-$CH_2NCH_2C\underline{H}_2$), 3.44 (s, 8H, $C\underline{H}_2COOBu^t$), 3.77 (s, 2H, bipy-$C\underline{H}_2$), 7.42 (m, 1H, Ph), 7.51 (m, 2H, Ph), 7.67 (m, 2H, Ph), 7.84 (dd, 1H, ^3J 8.4 Hz, ^4J 2.4 Hz, H-4), 8.02 (dd, 1H, ^3J 8.4 Hz, ^4J 2.4 Hz, H-4'), 8.38 (d, 1H, ^3J 8.4 Hz, H-3), 8.46 (d, 1H, ^3J 8.4 Hz, H-3'), 8.61 (d, ^4J 2.4 Hz, H-6), 8.91 (d, ^4J 2.4 Hz, H-6'). **ESI-MS** (acetonitrile), *m/z*: 804.48 $(M+H)^+$.

1,1,7,7-Tetrakis(carboxymethyl)-4-[(5′-phenyl-2,2′-bipyridine-5-yl)methyl]-1,4,7-triazaheptane (11). Ester **10** (0.48 g, 0.6 mmol) was dissolved in 5N hydrochloric acid (20 ml) and the resulting mixture was stirred at room temperature overnight. Solvent was removed under reduced pressure. The residue was washed with dry acetonitrile (10 ml) and dried under vacuum. To the residue hydrochloric acid (11N, 20 ml) was added and the resulting mixture was stirred at room temperature for 2 h. Solvent was removed under reduced pressure. Dry acetonitrile (25 ml) was added to the residue and the resulting mixture was stirred at room temperature for 8 h. Resulting precipitate was filtered off, washed with dry acetonitrile and dried under vacuum. Yield 0.35 g (0.46 mmol, 76%). Found, %: C 45.30, H 5.54, N 9.91, Cl 16.37. $\mathbf{C_{29}H_{33}N_5O_8*3.5HCl*3.1H_2O}$. Calculated, %: C 45.65, H 5.64, N 9.18, Cl 16.26.

Eu*11. Ligand **11** (75 mg, 0.1 mmol) was dissolved in water (10 ml). NaOH (30 mg, 0.75 mmol) and then $EuCl_3*6H_2O$ (37 mg, 0.1 mmol) were added to that solution and the resulting mixture was stirred at room temperature for 2 h. Solvent was removed under reduced pressure, the product was extracted from the residue with hot methanol (3 x 20 ml). Methanol was removed under reduced pressure; the product was dried under vacuum. Yield 66 mg (0.079 mmol, 79%). Found, %: C 40.98, H 4.33, N 7.95. $\mathbf{C_{29}H_{29}EuN_5NaO_8*5H_2O}$. Calculated, %: C 41.44, H 4.68, N 8.33. **ESI-MS** (water), *m/z* (I (%)), found: 726.12 (79), 727.12 (31), 728.12 (100), 729.12 (31), 730.13 (5.9) $(M\text{-}Na)^-$; calculated: 726.12 (86), 727.12 (29), 728.12 (100), 729.13 (33), 730.13 (6.9).

Acknowledgements

This work was supported by Russian Science Foundation (Ref. # 15-13-10033).

References

1. Cotton, S. A.; Harrowfield, J. M. Lanthanides: Biological Activity and Medical Applications. Encyclopedia of Inorganic and Bioinorganic Chemistry (**2012**).

2. (a) Quici, S.; Cavazzini, M.; Marzanni, G.; Accorsi, G.; Armaroli, N.; Ventura, B.; Barigelletti, F. *Inorg. Chem*. **2005**, *44*, 529; (b) Foley, T. J.; Harrison, B. S.; Knefely, A. S.; Abboud, K. A.; Reynolds, J. R.; Schanze, K. S.; Boncella, J. M. *Inorg. Chem*. **2003**, *42*, 5023.

3. Kido, J.; Okamoto, Y. *Chem. Rev*. **2002**, *102*, 2357.

4. Aime, S.; Crich, S. G.; Gianolio, E.; Giovenzana, G. B.; Tei, L.; Terreno, E. *Coord. Chem. Rev*. **2006**, *250*, 1562.

5. (a) Thejo Kalyania, N.; Dhoble, S. J. *Renewable and Sustainable Energy Reviews* **2012**, *16*, 2696; (b) de Bettencourt-Dias, A. *Dalton Trans*. **2007**, 2229.

6. (a) Hagan, A. K.; Zuchner, T.; *Anal. Bioanal. Chem*. **2011**, *400*, 2847; (b) Hovinen, J.; Guy, P. M.; *Bioconjugate Chem*. **2009**, *20*, 404.

7. Armelao, L.; Barigelletti, F.; Accorsi, G.; Cavazzini, M.; Tondello, E. *Coord. Chem. Rev*. **2010**, *254*, 487.

8. For example see: (a) Hanaoka, K.; Kikuchi, K.; Kojima, H.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc*. **2004**, *126*, 12470; (b) Pope, S. J. A.; Laye, R. H. *Dalton Trans*. **2006**, 3108; (c) Ye, Z.; Wang, G.; Chen, J.; Fu, X.; Zhang, W.; Yuan, J. *Biosensors and Bioelectronics* **2010**, *26*, 1043.

9. Couchet, J.-M.; Azéma, J.; Tisnès, P.; Picard, C. *Inorganic Chemistry Communications* **2003**, *6*, 978; (b) Baggaley, E.; Cao, D.-K.; Sykes, D.; Botchway, S. W.; Weinstein, J. A.; Ward, M. D. *Chem. Eur. J*. **2014**, *20*, 8898; (c) Ruloff, R.; van Koten, G.; Merbach, A. E. *Chem. Commun*. **2004**, *8*, 842.

10. (a) Costa, J.; Ruloff, R.; Burai, L.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc*. **2005**, *127*, 5147; (b) Dehaen, G.; Verwilst, P.; Eliseeva, S. V.; Laurent, S.; Vander Elst, L.; Muller, R. N.; De Borggraeve, W. M.; Binnemans, K.; Parac-Vogt, T. N. *Inorg. Chem*. **2011**, *50*, 10005.

11. Kozhevnikov, V. N.; Shabunina, O. V.; Kopchuk, D. S.; Ustinova, M. M.; König, B.; Kozhevnikov, D. N. *Tetrahedron* **2008**, *64*, 8963.

12. Prokhorov, A. M., Kozhevnikov, V. N.; Kopchuk, D. S.; Bernard, H.; Le Bris, N.; Tripier, R.; Handel, H.; Köenig, B.; Kozhevnikov, D. N. *Tetrahedron* **2011**, *67*, 597.

13. Platzek, J.; Niedballa, U.; Radeuchel, B. Patent US5514810(A) (**1996**), *Chem. Abstr*. **1996**, *125*, 87212.

14. (a) Ng, C.Y.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem*. **1979**, *18*, 2982; (b) Miranda, C.; Escart, F.; Lamarque, L.; Yunta, M. J. R.; Navarro, P.; Garca-Espaa, E.; Luisa Jimeno, M. *J. Am. Chem. Soc.* **2004**, *126*, 823.

15. Supkowski, R. M.; Horrocks, Jr, W. D. *Inorg. Chem. Acta.* **2002**, *340*, 44.

16. Clarkson, I. M.; Beeby, A.; Bruce, J. I.; Govenlock, L. J.; Lowe, M. P.; Mathieu, C. E.; Parker, D.; Senanayake, K. *New J. Chem*. **2000**, *24*, 377.

17. Maffeo, D.; Williams, J. A. G. *Inorg. Chim. Acta* **2003**, *355*, 127.

18. Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

19. Kozhevnikov, D. N.; Shabunina, O. V.; Kopchuk, D. S.; Slepukhin, P. A.; Kozhevnikov, V. N. *Tetrahedron Lett*. **2006**, *47*, 7025.

20. Kessler, M. A. *Anal. Chim. Acta* **1998**, *364*, 125; (b) Gunnlaugsson, T.; Leonard, G. A. Chem. Commun. **2005**, *25*, 3114.

21. Lakowicz, J. R. Principles of Fluorescence Spectroscopy. Plenum, New York, 2nd ed., **1999**.

22. Olea-Román, D.; Bélanger-Desmarais, N.; Flores-Álamo, M.; Bazán, C.; Thouin, F.; Reber, C.; Castillo-Blum, S. E. *Dalton Trans*. **2015**, *44*, 17175.